

Summer Scholar Report

Gas-Surface Reaction Dynamics Studied Using Molecular Beams

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During the summer of 2017, the process of steam reformation was studied, specifically, the rate-determining C-H bond cleavage step in steam reformation. The overall reaction which takes place in steam reformation is important, as it is the main industrially pathway for production of H₂ gas, a clean and powerful energy source that has the potential to replace other pollutant fuels currently used in the world, and is used in the production of synthetic fertilizer. The process which the Utz research group¹ focuses on is shown in Equation 1, which is performed over a nickel catalyst.



Equation 1. *Steam-reforming process*

The reason this reaction is known as a heterogeneous catalysis is as the catalyst is in a different physical state than the reagents and products in the reaction, as the methane and water are in gaseous states while the nickel is in solid state. This reaction is very important, as the hydrogen gas that is formed from the reaction seen in Equation 1 can be used then used in the Haber-Bosch reaction, which is seen in Equation 2. .



Equation 2. *Haber-Bosch process*

The hydrogen gas is reacted with nitrogen to produce ammonia; this ammonia can be used to produce synthetic fertilizers. This process is vital, as 48% of the world's population was supported and fed using synthetic fertilizers made using ammonia.² The world's population is also growing at a fast pace, so more fertilizer must be produced, meaning more hydrogen gas needs to be produced. The problem that arises is that the current industrial process used currently for steam reformation is not as efficient as it could be, and it is also costly. By studying the rate determining C-H bond cleavage step shown in Equation 3,



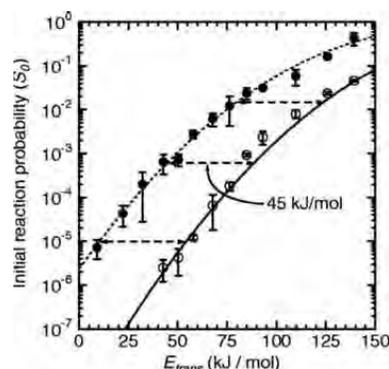
Equation 3. *Rate-determining step of heterogenous catalysis*

where the CH₃ and the H are adsorbed to the surface, the overall reaction can be made more efficient. Very few methane molecules that interact with the nickel catalyst react, as the reaction transition state has strict geometric and energetic requirements. To maximize the efficiency of adsorption of the methane on the nickel catalyst, industrially the methane gas is heated to high temperatures to maximize energy and is at very high pressures to increase collisions with the catalyst.

The machine built in the Utz lab which is used to study the reaction of methane on the nickel catalyst has four differentially pumped vacuum chambers; there is the source, where the methane gas is thermalized and the molecular beam is produced; the 1st differential chamber, which is where the methane molecules can be excited via an IR laser, the 2nd differential chamber, which is where beam analysis takes place, and the main chamber, which contains the nickel single crystal sample. To determine the exact nature of the interaction of methane with nickel, and to understand the restrictions on the transition state, methane can be produced with a specific kinetic and vibrational energy. These variables can give insight into the energetic and geometric restrictions on the minimum pathway to reactivity.

A mixture of methane gas, as well as lighter gases such as hydrogen, are pumped into the molecular beam, which is held at 40 psi, inside of the source chamber, held at a pressure of the magnitude 10⁻⁴ torr. The hydrogen gas is added into the mixture to bring down the average mass of the mixture, allowing for the kinetic energy of the methane to increase by increasing the velocity of the mixture of gases. Once the gases were thermalized, the molecular beam travels to the 1st chamber, where it is excited by the IR laser, then travels to the 2nd chamber, which then selects only the molecules that are traveling in a straight path to the nickel catalyst to pass the chamber.

Figure 1. *Sticking probability curves of methane on nickel with and without laser*



The IR laser is important as it excites the molecules vibrationally, meaning the molecules are vibrating in a specific orientation and carry a certain kinetic energy. Figure 1 above shows the sticking probability, or the likeliness of methane to react with the nickel surface, of methane that was excited by a laser compared to methane that was not. The curve on the right shows the reactivity of methane without laser excitation while the curve on the left shows methane in an excited state. The difference in energy in both curves is 45 kJ/mol, meaning the energy barrier of reaction decreases by that amount to react methane on nickel surface.

In order to carry out these experiments, however, the main chamber must be dry and not contain any gases. The machine is kept under vacuum at very low pressures, and any time that analysis is done, the main chamber must first be baked in order to get rid of any impurities in the chamber. Baking refers to wrapping the chambers up in heat tape, then wrapping everything in aluminum foil, in order to insulate the heat and prevent it from escaping. In the time spent in lab, there was a period of one to two weeks in which the machine was baking, so in this time period, the importance of the research was discussed, as well as, how everything was approached in lab. The parts of the chambers were discussed, how they were fixed, and any sort of troubleshooting that could be done during the bake was also done. One major difficulty that arose during this time was the position of the nickel crystal and where it was being held. In the main chamber, the crystal is attached to a small metal plate, which is then welded to six arms which hold the crystal in place. Heating filaments, which heat the chamber, are near the crystal; one of the filaments became loose, so the crystal hit the filament, causing the crystal to scratch. The crystal was removed from the chamber, breaking the vacuum, which resulted in another three-day bake. Afterwards, due to the position of the crystal changing, assistance was able to be given in order to find the optimal positioning of the nickel crystal in order to maximize reactivity of the methane on the crystal, as well as, to find optimal positions to analyze the amount of methane on the surface after reaction.

Table 1. *Positions of dosage beam, Auger Electron gun, and the sputter gun 7/11/17*

Positions	7/11/2017		
Axes	Dose	AES	Sputter
X	0.885	0.2	0.1
Y	0.65	0.5125	0.65
Z	2.213	0.8375	2.05
θ	2°	235°	160°

Table 1 above shows the positioning of the crystal in regard to dosage, Auger Electron spectroscopy, and the sputter gun. Auger Electron spectroscopy was done in order to get a model of the nickel surface, while the sputter gun was used to clean any impurities off of the crystal's surface. After finding the optimal position of the crystal in the main chamber, it was believed that the molecular beam could finally be run, as the nickel had the clean surface; however, after running a residual gas analysis using the Quadrupole Mass Spectrometer (QMS) seen in Figure 2 below, it could be seen that the chamber had a large peak at 19 m/z, indicating the presence of fluorine in the main chamber.

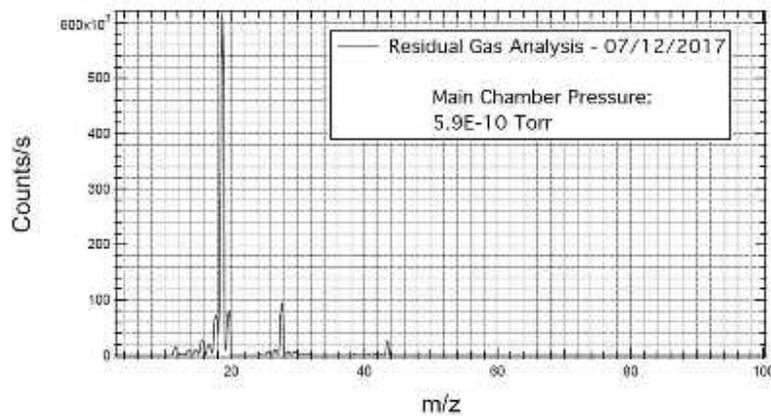


Figure 2. Gas analysis of the main chamber on 07/12/2017

This problem could have stemmed from different problems; since the chamber had been recently baked, there could have been a possibility that there was a technological malfunction, causing the reading above. Historically, the data shows that after baking, the residual gas analysis should resemble the graph shown in Figure 3.

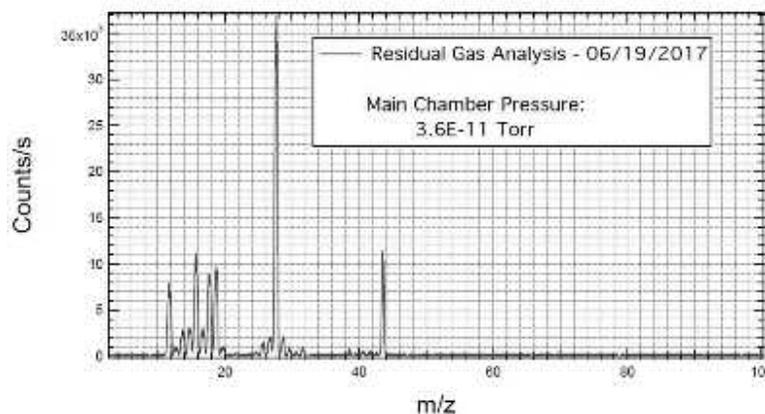


Figure 3. Gas analysis of the main chamber on 06/19/2017

Though there were many issues in terms of equipment, the skills that were gained during the summer are priceless, as being able to work on a problem hands-on is a valuable skill to have. This also shows that science does not always go as expected, and there are always roadblocks which you must face, and it is necessary to take on the roadblocks without giving up.

I would like to acknowledge the Utz research group at Tufts University for allowing me the opportunity to be in lab with them, as well as for teaching me many new and interesting techniques that I would not be able to be exposed to in other situations. I would also like to thank my research advisor Professor Del Sesto for introducing me to an interesting field in science, as well as introducing me to a great group of people at Tufts University.

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